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Intermolecular force constants in the condensed phase: ClCN and BrCN

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A simple linear lattice theory is used to calculate intermolecular force constants of liquid and crystalline ClCN and BrCN. For liquids, the obtained values conform to earlier predictions. For solids the values of intermolecular force constants along the chain are calculated and the results are in accord with the findings of nuclear quadrupole resonance studies and crystal structure analysis which indicated covalent character of intermolecular bonding along the chain.

1 Introduction

In the condensed phase intermolecular forces are strong enough to cause noticeable modification in the spectra when compared with the gaseous phase (Mitra 1962). The changes occur in the following way—(1) change in vibrational frequency, occasionally accompanied by change of intensities (2) splitting of single bands and (3) appearence of news bands in the low frequency region. The last two effects arise chiefly from solid state properties. Frequencies of the new bands in the low frequency region may be used directly to obtain an idea about the strength of the intermolecular forces. Triatomic molecules like HCN (Ghosh 1975), ClCN and BrCN (Pezolet & Savoie 1971) form a linear chain system in the condensed phase. If the linear chain contains only one of the molecules of a crystallographic unit cell, there will be no optically active mode corresponding to rigid molecule intrachain lattice vibration; hence no direct information about the strength of intermolecular forces within a chain can be obtained. However, we (Ghosh 1975) have shown that in the case of hydrogen-bonded linear chain system of HCN the modifications in the intramolecular vibration frequencies can be used to obtain information about the strength of intermolecular forces. In this case, we have a distinct advantage arising from hydrogen bond in that only one bond C-H is appreciably perturbed while the other bond C ≡ N remains almost unperturbed by polymerisation. The cyanogen halides like ClCN and BrCN form (Pezolet & Savoie, 1971, Casabella & Bray 1958; Geller & Schawlow 1955; Heiart & Carpenter 1956) a similar linear chain system in condensed phases, but both XC(X = halogen) and CN bonds are modified in condensed phases although the changes in stretching frequencies are not very drastic. The nuclear quadrupole resonance on solid ClCN (Casabella & Bray 1958) and BrCN

(Geller & Schawlow 1955) revealed a certain degree of covalent character for intermolecular bonding and hence a strong intermolecular force along the chain Intensities of the band in the Raman spectra of liquid ClCN and BrCN also establish molecular association and polymetrisation in the liquid state (Pezolet & Savoie 1971). A dimermodel calculation (Pezolet & Savoie 1971) with Wilson's *G*-matrix shows that in the liquid state force constants for bonded CX and CN are slightly modified as compared to free CX and CN, while there is appreciable intermolecular bonding In the solid state, however, no value of intermolecular force constant along the chain has been predicted earlier In the present study, we apply a linear chain model to calculate intermolecular force constants for both liquid and solid phases of ClCN and BrCN

2. Theory

Liquid Phase

Since the Raman spectra in the liquid phase of ClCN and BrCN show that an appreciable number of molecules are associated (Pezolet & Savoie 1971), for these associated molecules we assume an infinite triatomic linear chain (with neglect of edge effects) We are concerned with those polymer vibrations which interact with long wavelength radiation in the infrared and Raman spectroscopy. Hence wave number $q = 0$; atomic displacements in each unit cell will be identical and in a linear chain model one of the modes will correspond to uniform translation of the chain unit cell The two optically active frequencies satisfy the following (Ghosh 1975)

$$\lambda_1+\lambda_2 = K_1(\mu_X+\mu_C)+K_2(\mu_C+\mu_N)+K_X(\mu_N+\mu_X), \qquad \ldots \quad (1)$$

where $\lambda_i = 4\pi^2c^2\nu_i^2$ $(i = 1, 2)$, c is the velocity of light, ν_1 and ν_2 are frequencies (in cm^{-1}) of the bonded C—X and C ≡ N stretching modes respectively, μ's are reciprocals of masses of different atoms, K_1 and K_2 are intramolecular force constants for bonded CX and CN and K_X is intermolecular force constant For free molecules $K_X = 0$, if λ_i^f, K_i^f denote the corresponding terms for gaseous phase then

$$\lambda_1^f + \lambda_2^f = K_1^f(\mu_X+\mu_C)+K_2^f(\mu_C+\mu_N). \qquad (2)$$

from eqs (1) and (2) we can write

$$K_X = \frac{\Delta K_1(\mu_X+\mu_C)+\Delta K_2(\mu_C+\mu_N)-(\Delta\lambda_1+\Delta\lambda_2)}{(\mu_X+\mu_N)} \qquad (3)$$

where $\Delta K_i = K_i^f - K_i$ and $\Delta\lambda_i = \lambda_i^f - \lambda_i$ We have assumed nearest neighbour approximation In a molecular lattice, intermolecular binding being very weak, second nearest neighbour forces are important only for intra-molecular binding. This will introduce one extra term connecting the displacements of atoms X

and N In a dimer model calculation Pezolet & Savoie (1971) introduced a term corresponding to CX, CN interaction which could account for the second nearest neighbour force But a recalculation of force constants following Pezolet & Savoie (1971) with zero interaction force constants shows that although the values of K_1 and K_2 change slightly for both free molecules and dimers the values of ΔK_1 remain almost the same (table-1). This justifies our assumption of nearest neighbour approximation. Together with the experimental frequencies and data in table 1 formula (3) yield intermolecular force constants (table 2).

Table 1. Calculation of stretching force constants for gas molecules and dimers

Molecular system		Force constants (mdyn/Å) for K_1 (free)		K_1 (bonded)		K_2 (free)		K_2 (bonded)		K_x	
		Ref. 3	This work	Ref 3	This work	Ref 3	This work	Ref 3	This work	Ref. 3	This work
ClCN	(gas)	4 99	4 96			16 81	17 38				
ClCN	(dimer)	5 17	5 15	5 08	5 05	16 55	16 80	16 40	16 56	0 1	0 1
BrCN	(gas)	4 15	4 12			16 87	17 10				
BrCN	(dimer)	4.10	4.05	3 85	3.80	16.75	17 05	16 50	16 75	0 15	0 15

(a) assumed to be the same as in Pezolet & Savoie (1971)

Table 2 Data concerning atomic positions in the unit cell

Intrachain distances (Å)			Interchain distances (Å) (shortest)		
	ClCN[a]	BrCN[b]		ClCN[a]	BrCN[b]
X—C	1 57	1 79	X -X	3 87	4.01
C N	1 16	1 15	X—N	3 70	4.64
N—X	3 01	2 87	N- C		3 70
			N—N		4 0

(a) Heiart & Carpenter (1956).
(b) Geller & Schawlow (1955).

Solid Phase

Cyanogen chloride (Heiart & Carpenter 1956) and cyanogen bromide (Geller & Schawlow 1955) have isomorphous crystal structures, the crystals are orthorhombic (space group D_{2h}^{13}-Pnmm) with two molecules per unit cell. The unit cell parameters are $a = 5.68$, $b = 3.98$, and $c = 5.74$Å for ClCN and $a = 6.02$, $b = 4.12$

and $c = 5.80$ Å for BrCN; the molecules are arranged in infinite linear chains parallel to the c-axis. A pair of chains arranged antiparallel to each other contribute one molecule each to the unit cell (Fig. 3(b) in (Geller & Schawlow, 1965); the molecules are in positions $\pm(\frac{1}{4},\frac{1}{4},Z)$. Crystal structure analysis for BrCN further show that the distance between *N* atom of one molecule and Br atom of the next molecule in the same chain is 2.87Å, whereas the sum of the van der Waals radii of Br and *N* atoms is 3.45Å, the distances between different atoms in the neighbouring chains are also large compared to the corresponding intrachain distances (table 2). Hence the intermolecular binding along the chain is much larger than the binding between neighbouring chains.

Since the factor group is isomorphous with the D_{2h} point group, a factor group analysis (Bhagavantam & Venkatarayudu 1948) with D_{2h} character table shows that the eighteen normal modes of vibration may be classified in the following way : internal vibrations consisting of stretching $(2A_g+2B_{1u})$ and bending $(B_{2g}+B_{3g}+B_{2u}+B_{3u})$ modes, external vibrations consisting of acoustic $(B_{1u}+B_{2u}+B_{3u})$ modes, translatory lattice $(A_g+B_{2g}+B_{3g})$ modes and rotatory lattice $(B_{2g}+B_{3g}+B_{2u}+B_{3u})$ modes. As we are interested only in the vibrations along the chain we construct symmetry co-ordinates for displacements along *z*-axis (table 4). These co-ordinates show that the stretching vibrations of the two molecules are either in phase (A_g) or out-of-phase(B_{1u}). The frequencies of the corresponding Raman (Pezolet & Savoie 1971) and infrared (Freitag & Nixon 1956; Bandy *et al* 1970) active modes are almost identical, this indicates very little effect of a second molecule inside the unit cell on the intramolecular vibrations. While $S_6{}^{B}{}_{1u}$ is a translatory interchain lattice (acoustic) mode, $S_3{}^{A}{}_{g}$ is translatory interchain optically active lattice vibration. Frequency (Pezolet & Savoie 1971) for this T_2(Ag) mode yields force constants of the order of 0.1 mdyn/Å for ClCN and lower than this value for BrCN. Since the intermolecular interactions within a chain even in the liquid phase are stronger than this, we expect an intermolecular intrachain coupling much larger than the interchain coupling in the solid phase. For these reasons, in the present study we assume an infinite triatomic linear lattice structure for an isolated chain; the two stretching frequencies are given by either Raman (*g*) or infrared (*u*) active modes which will be identical in the absence of interchain coupling and there is no pure translational optic mode along the chain. Hence both the symmetric and asymmetric stretching frequencies will satisfy eqns. (1) and (3). Since the change in intramolecular force constants ΔK_1 is caused by molecular association, intramolecular force constants of bonded *CX* and *CN* for associated molecules in the liquid phase are assumed to be approximately the same as for associated molecules in the solid phase. The error involved in this assumption is not very large because the strength of intramolecular binding is determined largely by whether a group is free or bonded and not by whether the bonded group belongs to a dimer or a higher polymer. Intermolecular force

constants are evaluated (table 3) using data for ΔK_i from Table 1 and experimental frequencies for Raman (Pezolet & Savoie 1971) and infrared (Freitag & Nixon 1956, Bandy *et al* 1970) active modes

Table 3 Calculation of intermolecular force constants in liquid and crystalline ClCN and BrCN.

For ClCN[a](free) $\nu_1^f = 714$ cm^{-1} $\nu_2^f = 2219$ cm^{-1}

For BrCN[a](free) $\nu_1^f = 575$ cm^{-1} $\nu_2^f = 2200$ cm^{-1}

Molecular system	Temperature °C[d]	Frequencies[b] (cm^{-1})		Force constants (mdyn/A)		
		ν_1	ν_2	ΔK_1[c]	ΔK_2[c]	K_λ
Liquid ClCN	7	720	2200	−0 9	0.43	0.12
Solid ClCN	− 70	736	2209	0 9	0 43	0 49
	−180	734	2209	-0 9	0 43	0 48
	−195	736	2210	−0 9	0 43	0 52
Liquid BrCN	54	554	2181	0.32	0 35	0 26
Solid BrCN	35	574	2190	0 32	0.35	0 70
	-180	573	2193	0.32	0 35	0 78
	−195	573	2190	0.32	0 35	0 69

(a) from Freitag & Nixon (1956)

(b) stretching frequencies (A_g) from Pezolet & Savoie (1971)

(c) see text and Table-1

(d) ClCN (mp −6 5°C, bp 12 6°C) and BrCN(mp 51 3°C, bp 61.3°C)

Table 4. Symmetry co-ordinates for $q = 0$ modes

Symmetry	Symmetry co-ordinates[a]
A_g	$S_1 = (Z_{1X}-Z_{1C})-(Z_{2X}-Z_{2C})$
	$S_2 = (Z_{1C}-Z_{1N})-(Z_{2C}-Z_{2N})$
	$S_3 = (Z_{1X}+Z_{1C}+Z_{1N})-(Z_{2X}+Z_{2C}+Z_{2N})$
B_{1u}	$S_4 = (Z_{1X}-Z_{1C})+(Z_{2X}-Z_{2C}$
	$S_5 = (Z_{1C}-Z_{1N})+(Z_{2C}-Z_{2N})$
	$S_6 = (Z_{1X}+Z_{2C}+Z_{2N})+(Z_{2X}+Z_{2C}+Z_{2N})$

(a) Z_{1X}, Z_{2X} etc correspond to the two different molecules in the unit cell, the co-ordinates are to be multiplied by appropriate normalization constants

3 Discussion

Intermolecular force constants obtained for the liquid phase conform to the values assumed (Pezolet & Savoie 1971) earlier on the basis of far-infrared band of liquid ClCN and the splitting of ν_1 mode in liquid BrCN. For solids the obtained

values are approximately three to four times larger than in liquids. In fact intermolecular coupling in the liquid should indeed lead to a strong coupling along the chain in the solid phase The values of K_r in solids is consistent with the relatively short distance (Table 2) between the ends of adjacent molecules along the chain and the reported relative intensity (Pezolet & Savoie 1971) of the $\nu_1(^{37}Cl)$ stretching mode as compared to $\nu_1(^{35}Cl)$. Thus intermolecular bonds may indeed have a certain amount of covalent character The Mossbauer study (Pasternak & Sonnino 1968) of solid ICN does not show an appreciable covalent character of intermolecular bonding, nevertheless the situation need not be essentially the same in ClCN and BrCN

We have employed both symmetric and asymmetric stretching frequencies for calculation of intermolecular forces Bond-bending modes will correspond to transverse displacements of atoms in the chain. The two well-separated peaks for B_{2g} and B_{3g} species (Pezolet & Savoie 1971) clearly demonstrate the anisotropy of crystalline field this is also evident from the unit cell parameters Then a similar calculation of intermolecular force utilising the bond-bending modes will require using a mode with complete crystal unit cell with two molecules This model should accommodate two interchain force constants in view of the anisotropy of the crystal field in the two perpendicular directions This work, based on an isolated chain model, is aimed at finding intermolecular force along the chain in both liquid and crystalline phases.

Since the intramolecular stretching frequencies are very little perturbed by temperature change, our values of K_r remain almost the same at all temperatures in the solid phase (table 3), this is expected because temperature change does not cause any crystallographic phase modification in the solid The constancy of $K_\perp$ values over wide temperature range (table 3) allows us to extrapolate the result to the melting point in the solid phases. Thus the values of $K_\perp$ below and above the melting point differ sharply characterising the phase transition (Ghosh 1975) In liquids, however, it is expected that intermolecular force should decrease with increasing temperature and vanish at the boiling point. In the absence of data in the liquid phase at different temperatures this result could not be checked

Thus on the basis of our model Raman and infrared experiments may also be interpreted to predict strong intermolecular binding along the chain in condensed phases of ClCN and BrCN which corroborates the interpretations of nuclear quadrupole resonance experiments and crystal structure analysis, notwithstanding the results of Mossbauer study in solid ICN

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